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***In situ* environmental transmission electron microscope investigation of NiGa nanoparticle synthesis**

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In an energy system based around decentralized hydrogen production, methanol synthesis under lower pressure conditions could be a way to store hydrogen on location. In the search of catalysts that might open up new process, conditions studies based on density functional theory (DFT) calculations have predicted a nickel gallium alloy to be active for this reaction [1]. NiGa catalysts prepared by incipient wetness impregnation on a high surface area silica support (Saint-Gobain NorPro), using a solution of nickel and gallium nitrates have shown very promising results [2]. This work presents detailed Environmental Transmission Electron Microscope (ETEM) investigations of synthesis of NiGa nanoparticles on a thin film support.

Samples were prepared by dissolving $\text{Ni}(\text{NO}_3)_2$ and $\text{Ga}(\text{NO}_3)_3$ in a Ni:Ga ratio of 5:3 in millipore water. The solution was subsequently dispersed on transmission electron microscope (TEM) sample grids. The sample grid was then mounted in a TEM heating holder and inserted in a FEI Titan ETEM with imaging C_s corrector as well as facilities for *in situ* gas reactions [3]. The ETEM was operated at 300 kV. The synthesis was performed *in situ* in a H_2 flow of 2 Nml/min at a pressure of 130 Pa. The reaction was investigated from room temperature (RT) to 660°C by subsequently obtaining bright field TEM images, diffraction patterns (DP), High Resolution TEM (HRTEM) images, and Electron Energy Loss Spectroscopy (EELS) data.

Figure 1 shows bright field images of the sample during synthesis. The dispersed nitrate salts (A) starts to decompose around 300 °C (B). From 400 °C to 660°C (C) NiGa nanoparticles are formed. The particle diameter at 660°C was between 5 nm and 20 nm. From HRTEM and DP it is observed that the nanoparticles are crystalline.

Figure 2(A) shows a particle at 660°C with two overlapping crystal domains. The insets show the fast fourier transform (FFT) of the overlapping crystals (FFT1) and single crystal area (FFT2), respectively. The FFT2 resembles the orthorhombic Ni_5Ga_3 viewed along the $[1\ 1\ -4]$ zone axis [4]. Figure 2(B) shows EELS of a single particle at 660°C. Both Ni and Ga edges are observed in the spectra. Quantification of Ni:Ga ratio is hampered by the presence of the Ni L_1 edge.

The ETEM experiments have been supported by complementary *in situ* X-Ray Diffraction (XRD) measurements on synthesis of Ni_5Ga_3 catalyst on a high surface area silica support prepared by wet impregnation [2]. Although the *in situ* XRD was performed at significantly higher H_2 flow (40 Nml/min) and pressure (100 kPa) the complimentary data correlates with the main temperature dependence of phase and structure and shows formation of the Ni_5Ga_3 phase for temperatures higher than 300°C.

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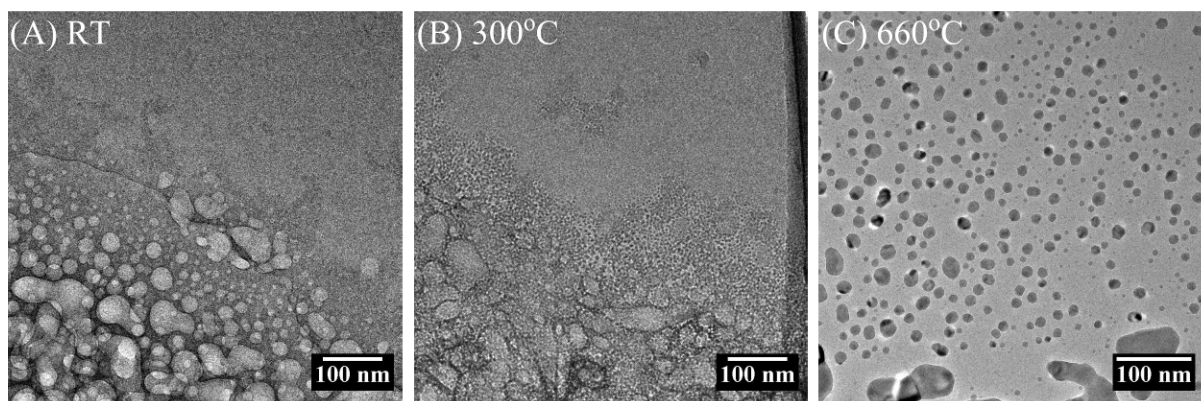


Figure 1. Bright field images of the sample during *in situ* synthesis in a H_2 flow of 2 Nml/min at a pressure of 130 Pa.

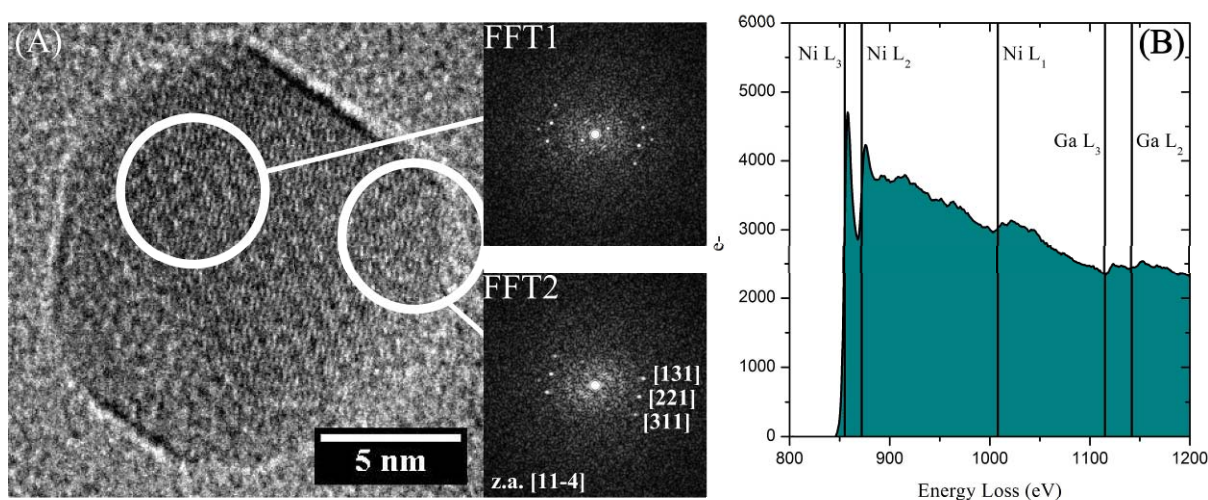


Figure 2. shows HRTEM image (A) and EELS (B) of a NiGa nanoparticle at 660°C in a H_2 flow of 2 Nml/min and at a pressure of 130 Pa. The insets in (A) show the FFT of two different parts of the particle (FFT2 zone axis [11-4]). The lines in (B) indicate Ni and Ga energy-loss edges.